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JPL

ADVANCED ENERGY STORAGE FOR SPACE APPLICATIONS

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ABSTRACT

NASA is planning a number of exciting space science and space exploration missions into the early 21st century. Most of these missions are mass, volume and cost critical and hence require batteries with high specific energy and energy density. State-of-the-art Ag-Zn and Ni-Cd batteries are too heavy and bulky for many of these future missions. To meet these challenges JPL is developing a number of advanced batteries under a NASA sponsored program. The advanced batteries presently under development are: 1) $Li\text{-}SOCl_2$ cells, 2) secondary lithium cells 3) advanced metal hydride cells and 4) high temperature sodium-nickel chloride cells. This paper gives an overview of the JPL Advanced Battery Program.

INTRODUCTION

NASA is planning a number of exciting space science and space exploration missions into the early 21st century to expand knowledge of the Earth, its environment, the solar system and the Universe, and to establish a permanently manned presence in space[1]. Most of the future space missions can be broadly classified into the following seven categories: 1) Launch Vehicles, 2) Near Earth Missions, 3) Planetary Spacecraft, 4) Surface Explorers, 5) Probes and Penetrators, 6) Planetary Surface Power, and 7) Mars and Venus Mission Power [2]. The power requirements of these missions vary from a few tens of watts to few kilowatts depending on the mission. Most of these missions are mass, volume and cost critical.

State-of-the-art (SOA) silver-zinc and nickel-cadmium batteries are too heavy and bulky for many of the future missions and further in some cases they do not meet the life and environmental requirements. These batteries also have poor charge retention properties. The major technology challenges in the battery area are: 1) reduce battery weight (2-3 times less than SOA batteries), 2) reduce battery volume (2-3 times), 3) increase operation life (> 10 years), 4) improve specific power and power density, 5) extend active storage/charge retention and 6) improve capability to operate under extreme environments. These improvements are projected to result in significant launch cost savings and increase in payload capability. No one single battery system can meet all these requirements. Some applications require high specific energy, and long active shelf life primary batteries (planetary probes, launch vehicles) and some others require high specific energy long life secondary batteries (planetary spacecraft and near earth missions). To meet these technical challenges, JPL is developing a number of advanced batteries under a NASA sponsored program. This paper gives an overview of the JPL Advanced Battery Program and summarizes the status of the development of various battery technologies at JPL.

JPL ADVANCED BATTERY PROGRAM OVERVIEW

The specific goals of the JPL program are to develop advanced primary and secondary batteries with 2-3 times the specific energy and energy density of SOA batteries, capable of providing greater than 2000 deep discharge cycles, and 5-10 year active life. The advanced batteries presently under development/assessment at JPL are: 1) primary $Li\text{-}SOCl_2$ cells, 2) ambient temperature secondary lithium cells 3) advanced metal hydride cells and 4) high temperature sodium-nickel chloride cells. A comparison of the specific energy and energy density of the SOA and advanced primary and secondary batteries are given in Figures 1 and 2 respectively. The performance envelope of the various SOA and advanced secondary batteries is given in Figure 3. From the data it can be seen that nickel-metal hydride and lithium batteries are suitable for low power applications and bipolar $Ni\text{-}H_2$ and sodium metal chloride batteries are suitable for applications requiring > 2 KW of power. Significant mass and cost advantages are projected with the use of these advanced batteries (Figure 4). The following [illegible] made at JPL to elate in these various battery technologies.

PRIMARY Li-$SOCl_2$ CELL PROGRAM

The lithium-thionyl chloride cell possess higher specific energy and energy density than any currently available primary cell. Other desirable features of these cells are: higher operating voltage, excellent voltage stability over 95% of the discharge, operating capability over a wide, operating temperature range, and exceptionally long active storage life. In view of these features NASA is considering to use these cells/batteries in several space missions such as planetary probes, penetrators, astronaut equipment, launch vehicles etc.

The prime objective of this program is to develop aerospace quality safe Li-$SOCl_2$ cells capable of delivering 300 Wh/kg at C/2 r-at-e and having an active shelf life, of greater than 5 years. Meeting this challenge, initiated in 1980, required an approach that included wor-k on the fundamental understanding of the reaction mechanisms, composition and physical structure of the electrodes and grids, role of the electrolyte, design of the cell and balance of materials, performance and safety/abuse tests followed by cell destructive physical analyses. The development of a high rate primary lithium thionyl chloride (Li-$SOCl_2$) electrochemical cell culminated in 1986 with the demonstration of a 300 Wh/kg 'D' Size' cell (Table I) capable of continuous discharge at the C/2 rate '3).

The resulting accomplishment was recognized by the Air Force Space Systems Division (AFSSD). AFSD awarded a contract to JPL to to develop 350/?50 Ah cells and batteries for the Centaur launch vehicle. The Centaur requirements are quite stringent and include performance tests, thermal, shock, safety, and vibration tests at high levels to meet the expected profiles, as well as six-year storage and pulse discharge at the C/3 rate. GTE Government Systems (later Yardney Technical Products) and Honeywell Power Sources Center (later Alliant Tech Systems) were selected by competitive procurement to design, fabricate, and test state,-c~f-ar-t high rate 150 Ah cells in I'base I of the task. Phase 2 of the development, was to select one contractor based on cell performance data and to develop a lightweight battery capable of meeting Centaur flight requirements. Near the end of the Phase 1 development, the Air Force discontinued the 150 Ah cell and battery development and focused on the demonstration of a 250 Ah Li/$SOCl_2$ battery for Centaur. Both contractors were selected for Phase 2 after cell critical design reviews (cI)Its) and battery preliminary design reviews (1'1)}<s).

Considerable progress was made by both contractors. Both contractors held successful cell and battery critical design reviews and manufacturing readiness reviews (MRRs). Both contractors delivered high rate cells and batteries that met or exceeded -,11 . 1 [illegible]

preliminary thermal requirements. Testing results indicated the suitability of the basic cell and battery designs for each contrac'tell- .

Yardney Technical Products initially developed a light weight titanium battery case design that met structural requirements but not thermal requirements. Subsequently Yardney with the assistance from JPL, developed and tested an aluminum housing for the battery. An Aluminum DET-3 battery, (Figure 5) based on a JPL suggested design and weighing 79 pounds successfully completed shock and vibration testing without overheating Cell performance, calorimetry, and pressure testing were completed. Battery qualification was initiated. Two batteries, completed environmental dynamics, one battery completed heater safety, life and prelaunch testing, one battery completed operational life testing, and thermal vacuum Worst Case, Hot - Payload Battery (WCH-PLB) testing was completed.

SECONDARY LITHIUM CELL PROGRAM :

Ambient temperature secondary lithium batteries have several intrinsic and potential advantages including higher energy density, longer active shelf life, and lower self discharge over conventional Ni-Cd, Pb-acid and Ag-Zn batteries. Successful development of these batteries will yield large pay-offs such as 2-3 fold increase in energy storage capability and a longer active shelf life of 2 to 4 years over Ni-Cd. A detailed analysis of the strengths and weakness of secondary lithium cells has indicated that these cells are most suitable for small spacecraft applications requiring less than 1 kW power. Secondary lithium batteries are presently being considered for a number of advanced planetary applications such as: planetary rovers (Mars Rover, Lunar Rover), planetary space craft/probes (MESUR, AIM, ACME, Mercury Orbiter) and penetrators. These batteries may also be attractive for astronaut equipment, and Geo-SYN spacecraft.

Secondary lithium cells presently under development in United States, Europe and Japan. These batteries can be classified into two groups based on the type of electrolyte employed: 1) liquid electrolyte batteries and 2) polymer electrolyte batteries. Both these types of batteries employ lithium metal as the anode material. A number of materials such as TiS_2, MoS_2, MoS_3, $NbSe_3$, V_2O_5, V_6O_{13}, $Li_{1+x}Mn_2O_4$, $Li_{1+x}V_3O_8$, $Li_{1-x}CoO_2$ and $Li_{1-x}NiO_2$ were evaluated as candidate cathode materials. During discharge of the cell, lithium metal is oxidized into lithium ions at the anode and lithium ions undergo an intercalation reaction at the cathode. During charge reverse processes occur at each electrode.

Under a NASA Code C sponsored program JPL is developing ambient temperature secondary lithium cells for future space applications. The primary objective of this program is to develop rechargeable lithium cells with [illegible] moderatedepths of discharge (50 percent). The major R&D thrusts of this program are to improve cycle 1 ife and safety of these cells. The technical approach consists of: 1) identification of advanced electrode materials cathode) and elect.]-clyte:} :'~;~~Lid:l'~~]d solid polymer electrolytes) capable of high specific energy and long cycle life, 2) determination of the influence of design variables on cell performance and safety, and 3) development of prototype cells ant] 4) establishment of a performance data base. Four different types of lithium batteries were proposed for development under this program. They are : 1) lithium batteries with liquid organic electrolyte 2) lithium ion batteries with liquid organic electrolyte 3) lithium polymer batteries, and 4) lithium ion polymer batteries.

After a detailed assessment of a number of cathode materials., TiS_2 was selected in view of its intrinsic reversibility and high specific energy. Experimental 1 Ah Lithium - Titanium Disulfide ($Li-TiS_2$) cells containing a liquid organic electrolyte (developed at JPL) achieved more than 950 cycles at 50 percent depth of discharge[4] (Figure 6). These cells have a specific energy > 120 Wh/kg and can operate at two hour- discharge rate (C/2) (Figure 7). Work is in progress to scale up this technology to the 5 Ah cell size.

A carbonaceous material was identified as an alternate anode material. Use of this material is projected to improve the safety and cycle life, of the, secondary lithium batteries. This material was found to have a specific capacity of 200-250 mAh/gm at C/10-C/2 discharge rates [5] (Table 11). Work is in progress f-o develop 1 Ah lithium ion cells with metal oxide cathodes.

JPL has developed a number of polyether - based solid polymer electrolytes and gelled electrolytes since 1989[6&7]. Polyethyleneoxide (PEO) and polyacrylonitrile (PAN) polymers were investigated as the base! polymers. The polyether-based electrolytes have appreciable conductivity near 100°C anti show stable interfacial stability towards lithium. The gelled elect.rc]lytcs were found to have 10^{-3} S cm^{-1} conductivity even at room temperature. However, these gelled electrolytes are found to be reactive towards lithium and require modification to improve their stability towards lithium. Recently, JPL developed a composite solid polymer electrolyte with lithium transport number close to unity. This electrolyte is suitable for use at near 100°C and is projected to provide long cycle life. Some of the important properties of the solid polymeric electrolytes developed at JPL are given in Table 111. Work is in progress to transition this technology f1-om the materials level to the cell level.

S01)1 UM-METAL CHLORIDE CELL PROGRAM

A new class of high temperature, sodium rechargeable batteries based on transition metal chlorides as positive electrodes have emerged in the last decade [8] ...

systems are similar to the sodium-sulfur batteries in terms of anode half cell and the (high) energy densities. In addition, the use of solid metal chloride cathodes in basic chloroaluminate melts results in several significant advantages, including lower operating temperatures, improved safety and higher reliability. These batteries are suitable for large spacecraft that require in excess of 2 kW of power. and are ideal candidates for missions that require high operating temperature capability. JPL is presently considering these batteries for missions to planet Venus. This mission requires batteries that can operate at temperatures as high as 300-400°C.

The primarey objective of the JPL program is to conduct exploratory scientific studies on sodium metal chloride battery systems and determine their suitability for space applications. Based on the results of these studies a decision will be taken in 1994 to initiate an applied research program leading to the development of practical hardware for technology demonstration.

The research effort at JPL has focused mainly on understanding the basic electrochemical behavior of the metal chloride cathodes, i.e, in verifying the electrochemical reversibility, elucidating the reaction mechanisms, estimating the rate parameters and identifying the rate-limiting processes. Several transition metal chlorides have been evaluated for their electrochemical properties. The results obtained clearly indicate that $NiCl_2$ is intrinsically more reversible and stable in the electrochemical environment of the cell than the other cathode materials. Based on these results $NiCl_2$ was selected for further detailed assessment.

Experimental 2 Ah $Na/NiCl_2$ cells containing various additives were made and the cycle life performance of these cells was determined at 300° C (Figure 8). The purpose of this study was to determine effect of additives on the cycle life performance of these cells. The results obtained suggest that addition of small quantities of sulfur reduces the premature capacity loss and improved the cycle life performance[9]. Post mortem analysis of the cells revealed that there is a considerable agglomeration in the electrode during cycling in the absence of sulfur additive. The grain size has increased from an initial value of ~15 μ to 50-60 μ during cycling in the cell without additive. In the cells with the sulfur additive, on the other hand, the grain size was reduced to 5-10 μ. Addition of transition metals, especially Mn and Fe also appears to provide some degree of protection against such rapid capacity decline, though the effect is not as prominent as with sulfur. Work is in progress to assess the cycle life performance of this system.

NICKEL-METAL HYDRIDE CELL PROGRAM

Ni-MH system has twice the specific energy and energy density compared to the Ni-Cd charge methods are similar for both Ni/MH and Ni/Cd cells. Further, Ni-MH cells can tolerate overcharge and overdischarge. These cells do not develop significant pressure during cell operation. Both the electrode reactions in Ni/MH involve solid state reactions involving proton intercalation and de-intercalation. The absence of dissolution precipitate on reactions at the negative electrode eliminates the possible cell failure due to dendrite shorts. The metal hydrides cells are believed to be non-toxic and environmentally acceptable and therefore pose no problems in disposal.

A program with basic and applied research elements was initiated in FY 1993 at JPL. The main objective of the basic research element is to develop advanced metal hydride materials with improved specific capacity and electrochemical stability. The applied research element is aimed at assessing the technology of the SOA Ni-MH batteries and qualifying these batteries for space applications. Ni-MH cells will be procured from Gates and Eagle Pitcher industries and the cells will be evaluated for their electrical characteristics, cycle life performance, and operating temperature range.

SUMMARY AND CONCLUSIONS

JPL is developing a number of advanced batteries for future space applications under a NASA sponsored program. Some of the major accomplishments are:

1) Developed high rate 'D' size $Li-SOCl_2$ cells with a specific energy of 300 Wh/Kg for planetary applications. This technology was subsequently scaled to 250 Ah size, under an Air Force sponsored program for centaur launch vehicle applications.

2) Developed 1 Ah ambient temperature secondary $Li-TiS_2$ cells with a specific energy of 100 Wh/Kg and capable of delivering 1000 cycles at 50% DOD. Work is in progress to develop lithium ion cell technology.

3) Developed a number of polyether-based polymer and gelled electrolytes for use in lithium polymer batteries. Work is in progress to transition this technology from the materials level to the cell level.

4) Demonstrated the usefulness of sulfur additives to improve the cycle life performance of $Na-NiCl_2$ cells.

5) Assessment of Ni-MH cell technology for space applications is in progress.

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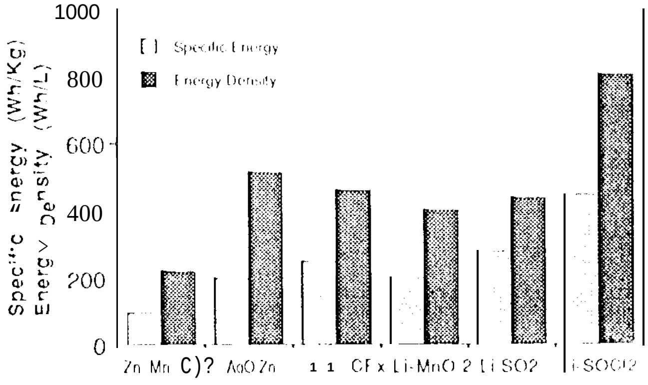


FIG 1 COMPARISON OF THE SPECIFIC ENERGY AND ENERGY DENSITY OF VARIOUS PRIMARY BATTERIES

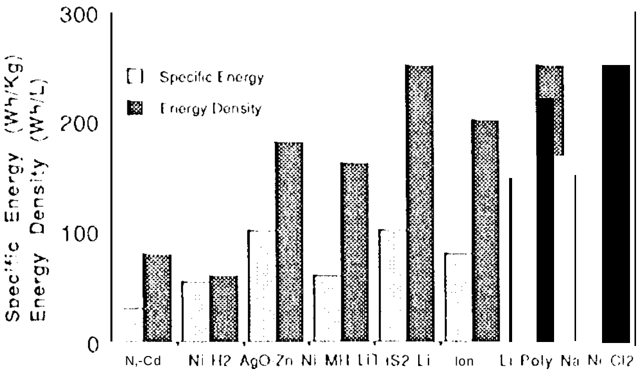
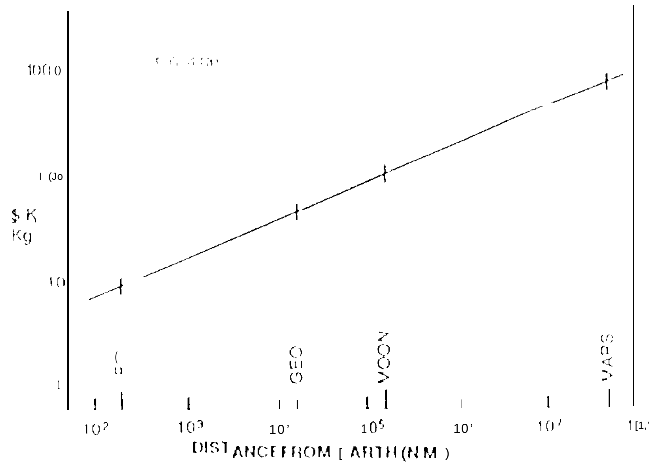
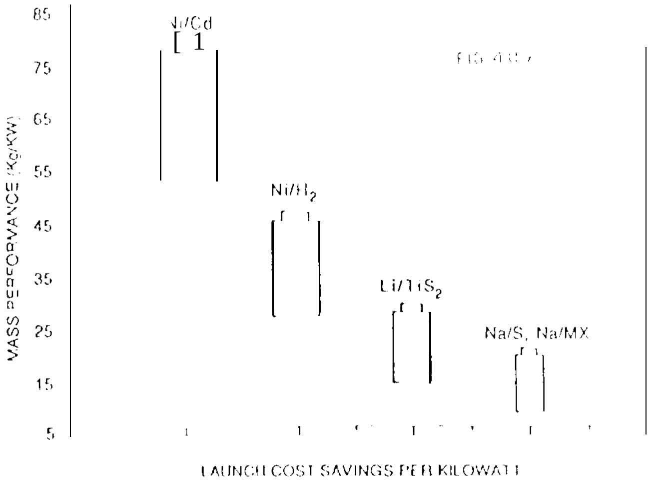


FIG. ? COMPARISON OF 1 t IE ENERGY DENSITY & SF'E CIFIC E NE RGY OF VARIOUS RECHARGEABLE BATTERIES.





MASS COST ADVANTAGE

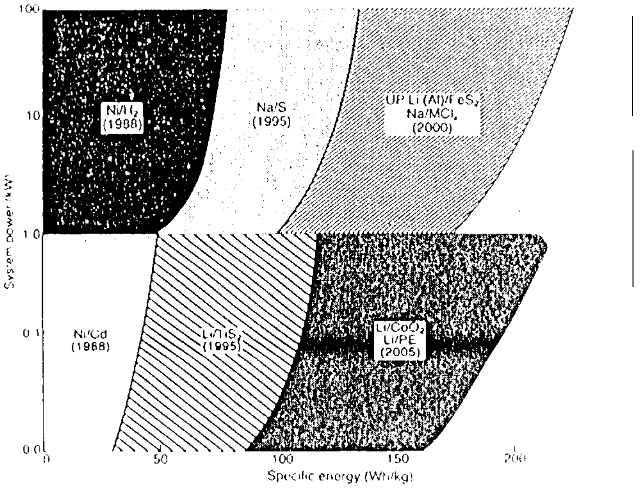


FIG. 3 ADVANCED RECHARGEABLE BATTERY PERFORMANCE ENVELOPE

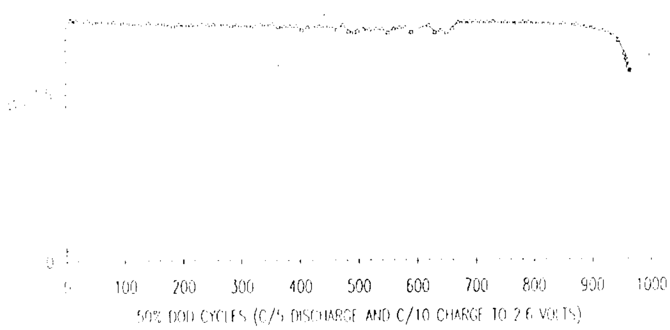
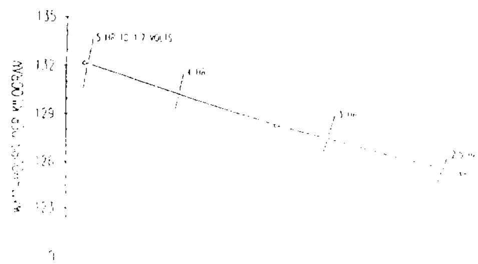


FIG. 6 CYCLE LIFE OF Li TiS2 AT 50% DOD



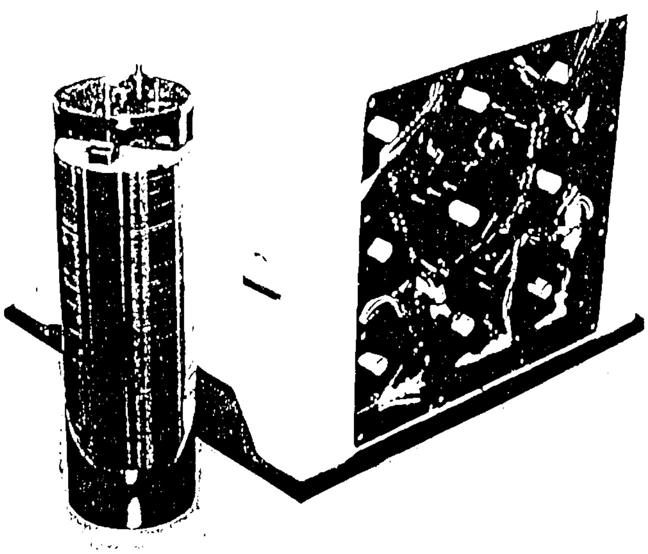


FIG. 5 Li-SOCl2 DET-3 ALUMINUM BATTERY

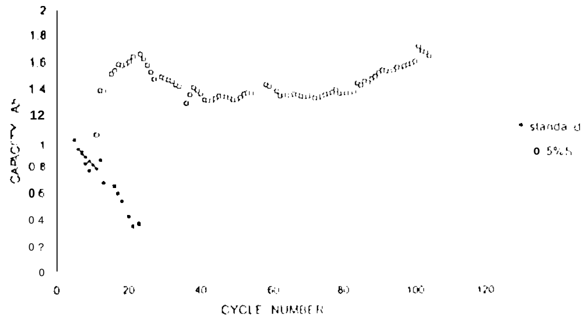


FIG 8 VARIATION OF CAPACITY OF 2 AH LOOSE SINTERED $NiCl_2$ IN THE ELECTROLYTE WITH NO ADDITIVE AND WITH 0.5 w% SULFURIC ACID

TABLE II. Rate Capability of Li out (C) and Li in (D) in Li_xC Anode

CURRENT (mA/cm²)	CAPACITY (mAh/gm)
0.167	235
0.333	214
0.667	208
1.000	200

TABLE I PERFORMANCE CHARACTERISTICS OF JPL's $Li\text{-}SOCl_2$ CELLS AT 70°F

CHARACTERISTIC	DISCHARGE RATE (A)		
	5	2	1
CAPACITY TO 2 0 V	11.6	111	12 0
OPERATING VOLTAGE	3 2	3 3	3 4
SPECIFIC ENERGY Wh/kg	317.0	311 0	343 0
ENERGY DENSITY Wh/dm^3	675 0	662 o	731 0

Table III. Properties of JPL Polymeric Electrolytes

Polymer Electrolyte	Conductivity $S\ cm^{-1}$	Lithium Transport Number
$PEO\text{-}12CR4/LiBF_4$	~ 5×10^{-3} at 100°C	0.3
$PAN+PC+LiBF_4$	1.5×10^{-3} at 20°C	NA
$PVF_2+PC+LiBF_4$	1.5×10^{-3} at 20°C	NA
ENVIBAR+EC+PC+ Li Imide	10^{-3} at 20° C	NA
Composite Electrolyte	~10^{-4} at 100°C	~1